Conformations of Poly(methyl methacrylate) and Its Degraded Forms upon Radiation

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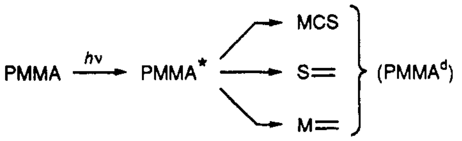
ABSTRACT: The radiation-induced decomposition of syndiotactic (st) and isotactic (it) poly(methyl methacrylate) (PMMA), containing $CH_2C(COOCH_3)(CH_3)$ units, to yield irradiation products (PMMA^d) resulting from hydrogen abstraction from α-methyl or methylene groups to form main chain (M=) or side chain (S=) double bonds is studied by conformational analysis. Relative minimum energy conformations of the st- and it-isomers of PMMA as free molecules are studied. The isomers of PMMA^d have relative minima in an overall linear (L) chain (assumed to be the form retained in the solid) as well as a global minimum in a bent (B) form (assumed to contribute to forms in solution). The impact of the change of a tetrahedral carbon atom to a trigonal carbon atom upon double bond formation on the conformational energy is fundamental to the understanding of the results. The experimental results are explained by the following theoretical observations. In reactions involving only overall linear conformations, side chain double bond formation is favored because of the resulting large increase in steric repulsion between polymer units in main chain double bond formation. In reactions proceeding to bent conformations, however, the decreased steric interaction yields both main and side chain double bond formation within 6.3 kcal/mol for the st-PMMA^d isomer and 2.2 kcal/mol for the it-PMMA^d isomer. Reactions on surfaces are assumed to be constrained to the overall linear conformation of the starting material, PMMA. Prevention of both M= and S= degradation products is desired for microlithographic applications. Increased solubility arising from main chain scission (MCS) is desired, and both M= and S= for that reason are undesirable with respect to resist sensitivity. It is proposed that the troublesome S= process can be attenuated or eliminated by replacing α-CH_3 with α-CF_3, thus enhancing the distribution of products toward MCS.

Introduction

Poly(methyl methacrylate) (PMMA) is used as a positive resist in advanced microlithography with electron beams, proton beams, X-rays, or ultraviolet light.[1] Irradiation of PMMA causes main chain scission (MCS), which is desired because it increases solubility in the exposed areas. Hydrogen abstraction from an α-methyl or methylene group also occurs upon irradiation, particularly with ultraviolet light,[2] producing carbon–carbon double bonds in either the main chain (M=) or a side group (S=) by cleavage of methyl ester groups but without causing main chain scission. Formation of M= and S= double bonds is undesirable because fragments of PMMA with substantially increased solubility are not produced. The extent of formation of each of the derivatives resulting from irradiation depends on the physical state of the PMMA. In solution all three products are observed, while in the solid, where two- and three-dimensional structures must be considered, MCS and S= predominantly are observed.[3] In summary, the PMMA is excited (*) and then undergoes decomposition (d) to several products:



In this work we study the conformational and binding energies of PMMA to gain insight into the formation and distribution of M= and S= products. The resulting information should enable us to propose modifications of PMMA that would increase the amount of main chain scission by reducing or, in the optimum case, eliminating double bond formation by hydrogen abstraction from α-methyl or methylene groups.

Choi et al.[2] have demonstrated that the number of methyl ester groups cleaved approximately equals the number of C=C bonds formed. Main chain scission was deduced by the reduced molecular weight[1] obtained from GC and GC–MS (for volatile fragments), FTIR, and HPLC experiments,[4] and the number of these scissions was determined by gel permeation chromatography.[2] The ratio of main chain scission to formation of M= and S= bonds was found to be 0.026 for UV and 0.293 for X-rays.[2] Consequently, degradation of the polymer to the M= and S= forms may be a significant problem in optimizing PMMA as a resist. Because main chain scission should only shorten the chain length, which increases its solubility, and not alter the overall structure and conformation of long segments in any other way, it is not considered in the present conformational analysis.

Our interest is to examine the conformations of syndiotactic and isotactic PMMA to understand the influence of stereochemistry on the ability to form double bonds upon irradiation in solution or, more importantly, in the solid state. A repeat unit of PMMA is defined as an enchained monomer unit of methyl methacrylate, $CH_2C(COOCH_3)(CH_3)$ (see Figure 1a). PMMA was studied in two conformations, syndiotactic (st-PMMA) and isotactic (it-PMMA) (Figure 1b,c). The products resulting from irradiation of st-PMMA which have a double bond in the main chain or to a CH_2 side group are illustrated in Figure 2. Molecular mechanics calculations are presented on isolated chains of PMMA in the various forms, and rationalizations for the products formed when PMMA is irradiated in the solid state and in solution are presented. Preference for S= over M= products is explained with molecular mechanics, and a proposal is presented for the synthesis of related polymers in which S= double bond formation can be attenuated or eliminated.

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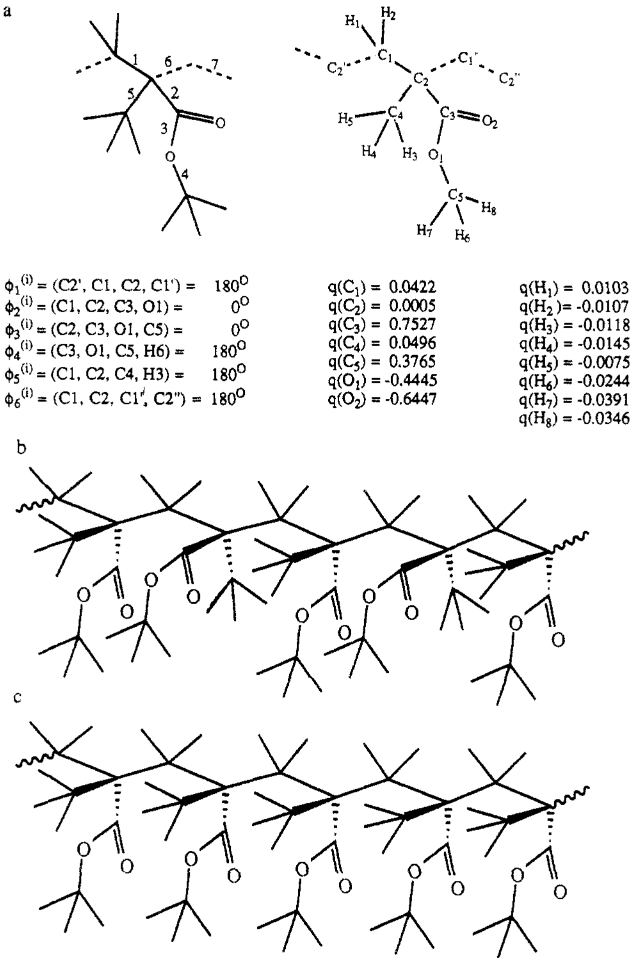
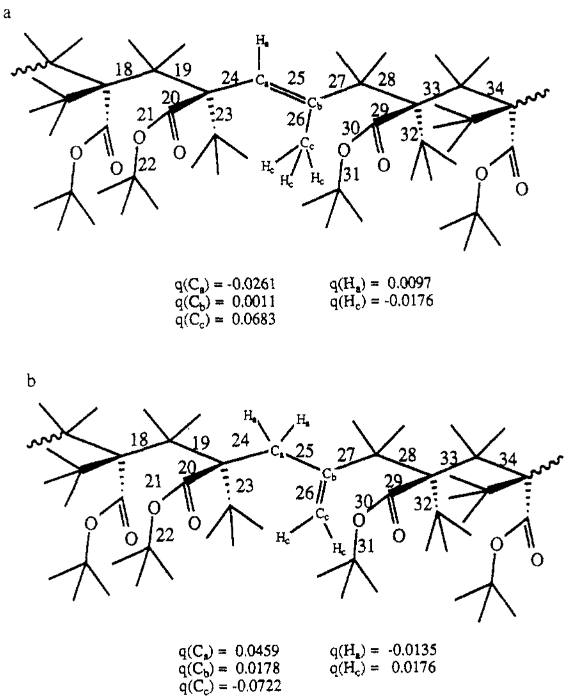


$\phi_1^{(i)}$ = (C2', C1, C2, C1') = 180°
$\phi_2^{(i)}$ = (C1, C2, C3, O1) = 0°
$\phi_3^{(i)}$ = (C2, C3, O1, C5) = 0°
$\phi_4^{(i)}$ = (C3, O1, C5, H6) = 180°
$\phi_5^{(i)}$ = (C1, C2, C4, H3) = 180°
$\phi_6^{(i)}$ = (C1, C2, C1', C2'') = 180°

$q(C_1)$ = 0.0422
$q(C_2)$ = 0.0005
$q(C_3)$ = 0.7527
$q(C_4)$ = 0.0496
$q(C_5)$ = 0.3765
$q(O_1)$ = -0.4445
$q(O_2)$ = -0.6447

$q(H_1)$ = 0.0103
$q(H_2)$ = -0.0107
$q(H_3)$ = -0.0118
$q(H_4)$ = -0.0145
$q(H_5)$ = -0.0075
$q(H_6)$ = -0.0244
$q(H_7)$ = -0.0391
$q(H_8)$ = -0.0346

Figure 1. Methyl methacrylate: (a) monomer with numbered bonds (left) and atoms (right), initial torsional angles, and net atomic charges; (b) the syndiotactic (st) polymeric form; (c) the isotactic (it) polymeric form.



(a)

$q(C_a)$ = -0.0261
$q(C_b)$ = 0.0011
$q(C_c)$ = 0.0683
$q(H_a)$ = 0.0097
$q(H_c)$ = -0.0176

(b)

$q(C_a)$ = 0.0459
$q(C_b)$ = 0.0178
$q(C_c)$ = -0.0722
$q(H_a)$ = -0.0135
$q(H_c)$ = 0.0176

Figure 2. st-PMMA with (a) a double bond in the main chain (M=) and (b) a double bond in the side group (S=) with numbered bonds and net atomic charges.

Computations

All computations refer to isolated chains. Standard bond lengths[5] (C-H, 1.08 Å; C-C, 1.54 Å; C-O, 1.36 Å; C=O, 1.23 Å; C=C, 1.40 Å) and bond angles (C-C-C, 112.0°; C-C-H, 109.5°; C-C-O, 109.5°; C-C=O, 120.0°; C-O-C, 109.5°) were used in all models. The molecules are constructed from methyl methacrylate repeat units (Figure 1) with alterations to represent the structures formed from PMMA upon irradiation as shown in Figure 2. The partitioning of the energy into nearest, next nearest, and more distant neighbor interactions was performed to demonstrate that the use of a polymer segment with more than four units eliminates end effects in the PMMA study. Hence, polymers containing nine repeat units were chosen to reduce the effect of long-range interactions and end group effects on the conformational energy when double bonds are introduced into the central polymer unit. Energies are reported in kcal for the 9-mer and in kcal/mol for the M= and S= products.

Optimization was performed with fixed bond lengths and bond angles but varying torsional angles. Therefore, calculations include interactions between all atoms not bonded through a common atom and changes in the torsional angles. The conformational energy is a sum of the steric (U), Coulombic (Q), and torsional (T) energies. The energy is minimized by rotating about the numbered bonds in Figures 1 and 2.

The steric energy is $U_{ij}(s_{ij}) = [A_{ij}/\rho_{ij}^6][1/s_{ij}^6 - 6/(ns_{ij}^n)]$, where $s_{ij} = r_{ij}/\rho_{ij}$ is the reduced distance, r_{ij} is the distance between the two atoms, and $\rho_{ij} = \rho_i + \rho_j$ is the sum of the van der Waals radii. $A_{ij} = -1.5\alpha_i\alpha_j I_i I_j/(I_i + I_j)$ is the London dispersion coefficient with atomic polarizabilities (α_i and α_j) and ionization potentials (I_i and I_j). These parameters are presented elsewhere.[6,7] The Coulombic energies are calculated with $Q_{ij}(r_{ij}) = q_iq_j/(\epsilon r_{ij})$, where the net charges are obtained from the MINDO/2[8] procedure and listed in Figures 1a and 2a,b. The sum is over all atoms i and j not bonded directly or bonded to a common atom. The macroscopic dielectric constant, ϵ, arises from the polarization of electrons and the orientational freedom of the molecules in response to an applied electric field. For example, the effect of each contribution is demonstrated by the change $\epsilon(H_2O) = 80$ to $\epsilon(\text{ice}) = 4$ because the rotating dipole contribution ceases. Studies in polymers[9] and crystals[10] suggest that a value of $\epsilon \approx 4$ is satisfactory. Studies of dielectric constants of ϵ = 1, 4, and ∞ were made,[11] but those for ϵ = 4 reported here encompass all the trends. The torsional energy is obtained as a sum for each bond with $T_b = [V_b/2][1+(\lambda_b/|\lambda_b|)\cos(\lambda_b\Phi_b)]$, where V_b is the barrier to rotation, λ_b describes the symmetry, and $\Phi_b = \phi_b^{(i)} + \phi_b$ is the torsional angle written as a displacement, ϕ_b, from the initial conformation, $\phi_b^{(i)}$, reported in Figure 1a. The parameters for the bonds are (bond, V_b, λ_b) = (CTE-CTE, 3.0, +3), (CTE-CTR, 0.001, +6), (CTR-OTE, 3.0, +2), (OTE-CTE, 3.0, +3), and (CTR-CTR, 50.0, -2), where CTE and CTR are tetrahedral and trigonal carbon atoms and OTE is a tetrahedral oxygen atom.

Discussion and Models

Various conformations were studied. The C=O was oriented all cis (c), all trans (t), or alternating cis-trans to the α-CH_3. The three studied, [tttt(t)tttt], [cccc(c)cccc], and [ctct(c)tctc], yield the minimum energy conformations reported in Table I. In this study nine polymer units are considered to eliminate end effects on the central polymer unit (indicated in parentheses) which undergoes the degradation indicated in the tables. The best conformation for each isomer is illustrated in the figures indicated in

Table I. Minimum Conformational Energies for a 9-Mer of the Various PMMAs[a]

I	E_u	$E_{L,M=}$	$E_{L,S=}$	$E_{B,M=}$	$E_{B,S=}$
	C=O to α-CH$_3$, [tttt(t or =)ttt]				
st	209.9	189.5	140.9	97.3	103.6
it	62.8	85.6	55.8	17.0	14.7
9/1L (it)	66.3 (3c)				
9/1R (it)	66.6				
	C=O to α-CH$_3$, [cccc(c or =)cccc]				
st	177.0 (3a)	165.9 (4a)	120.2 (4b)	80.9 (5a)	85.3 (5b)
it	84.2				
9/1L (it)	78.6				
9/1R (it)	79.1				
	C=O to α-CH$_3$, [ctct(c or =)tctc]				
it	50.6 (3b)	76.1 (4c)	35.6 (4d)	8.4 (5c)	6.2 (5d)
9/1L (it)	80.4				
9/1R (it)	78.5				

[a] The best unirradiated (u) and irradiated (L,M=; L,S=; B,M=; B,S=) conformations are shown in the figures indicated in parentheses. The energies are reported in kcal for the 9-mer.

Table II. Kink and Turn Angles (deg) in the Various PMMAs[a]

I	u	L,M=	L,S=	B,M=	B,S=
	C=O to α-CH$_3$, [tttt(t or =)ttt]				
st	3.1	9.5	3.5	45.0	76.8
it	4.5	5.7	14.5	48.9	35.1
9/1L	39.4 (3c)[b]				
9/1R	39.3				
	C=O to α-CH$_3$, [cccc(c or =)cccc]				
st	2.9 (3a)	3.0 (4a)	3.3 (4b)	45.0 (5a)	73.8 (5b)
it	4.2				
9/1L	42.1				
9/1R	42.1				
	C=O to α-CH$_3$, [ctct(c or =)tctc]				
it	4.0 (3b)	5.5 (4c)	20.0 (4d)	50.1 (5c)	35.2 (5d)
9/1L	39.7				
9/1R	39.4				

[a] The kink angle is calculated with vectors along adjacent pairs of polymer units. For the unirradiated PMMA, it is the average kink calculated with four sequential units, and for the irradiated isomers, it is the average through the double-bonded region calculated using six sequential units. The angle reported for the helices is the turn angle between two adjacent polymer units. [b] The best unirradiated (u) and irradiated (L,M=; L,S=; B,M=; B,S=) conformations are shown in the figures in parentheses.

parentheses adjacent to the global minimum. Several trends are apparent. First, all st-isomers with [cccc(c)ccc] are more stable than the all-trans conformation. Second, all it-isomers with alternating [ctct(c)tctc] are more stable than the all-trans case. Third, the it-PMMA in the [ctct(c)tctc] conformation is more stable than the 9/1 helix and the tighter 5/1 helix (not reported). The energy change for reorientation of the C=O from all cis to all trans for the st-isomer and alternating cis–trans to the all trans for the it-isomer is accomplished by differencing the energies reported in Table I and dividing by the appropriate number of bonds involved. The energy increase of 2–4 kcal/mol for all isomers summarizes the stability of all-cis st-isomers and alternating it-isomers. The energies in Table I are reported for a 9-mer to eliminate end effects and to represent the conformational change in the degraded region in the subsequent calculations of the energy differences (kcal/mol of double bonds formed) between the irradiated and unirradiated forms. The torsional angles are rotated in concert along the units. For example, angles 1, 2, 3, ..., 6 are repeated in 7, 8, 9, ..., 12, etc. in the same or opposite directions relative to the starting angles, depending on the isomer. For the products, all torsional angles in units 3, 4, 5, 6, and 7 are allowed to vary freely to permit flexibility in the degraded region. The overall chain conformation is important. In Table II the kink angles between two pairs of polymer units are reported along the chain for the unirradiated PMMA and adjacent to the double-bonded region in the irradiated products. We did not optimize the bond lengths and bending angles. Vacatello and Flory[12] find that it-PMMA has a lower conformational energy than st-PMMA, while our results show the reverse. However, we use the results consistently to interpret the trends in the relative energy changes as each of the st- and it-PMMAs undergo irradiation, that is, as the reaction region is altered. Vacatello and Flory[12] and Sundararajan[13] have performed statistical and conformational calculations to determine accessible regions of conformational space of the free molecule. They find mixtures of cis, trans, g^+, and g^- throughout the chain, conformational relative minima, with an a priori probability of a trans bond of 0.72 in it-PMMA and 0.89 in st-PMMA. We assume that the PMMA is adsorbed onto a surface and notice that the important free molecule conformations are low-energy ones which are already overall linear as the free molecule, and consequently, adsorption onto the surface is assumed to stabilize this conformation over the mixtures with g^+ and/or g^-. Introduction of slightly higher energy forms which are not overall linear, as found and used in the statistical studies,[12,13] are not considered in our study. Similarly, the low-energy helical conformations of it-PMMA, although close in energy to the overall linear forms, are not used because we assume that intimate contact with the surface preferentially stabilizes the overall linear form. In a paper concerned with a suggested unit cell for it-PMMA,[14] studies involving helical conformations have been reviewed. The most stable conformation is a 9/1 helix, reported in this paper, and it is not an acceptable candidate for adsorption on a surface.

The calculations were performed on the free molecule. Because the global minima of both starting isomers are linear, we assume that additional stabilization will occur in the solid or on the surface. In the degraded forms, one set of relative minima are overall linear (or reasonably so) polymers. We assume that the effects of main and side chain double bond formation are sufficiently local to prevent long-range conformational disruptions of the chain in the solid or on the surface after irradiation of the PMMA. In contrast, in solution, one may assume that the global minima of the bent forms can be attained after irradiation. These ideas are used throughout the paper to focus attention on a mechanism in which linear forms play the principal role in the solid but the bent forms are accessible in solution.

st-PMMA yields a minimum energy conformation with a straight chain or linear conformation (L) shown in Figure 3a in agreement with low-energy ion scattering spectroscopy and angle-resolved X-ray photoelectron data.[15] If an axis is defined through successive methylene groups, then the molecular axis is nearly linear (with a kink of only 3°), and the backbone of the polymer exhibits alternating left- and right-handed stereoplacements which are mirror images of each other. The kink is the angle determined by the dot product of vectors defined by successive backbone atoms [$C_\alpha(i)$, $C_\alpha(i+1)$] and [$C_\alpha(i+1)$, $C_\alpha(i+2)$]. This is used to quantify the curvature of the backbone.

it-PMMA yields two minimum energy conformations. The first, shown in Figure 3b, forms an overall average linear chain (with a kink of 4°) as noted from low-energy ion scattering spectroscopy and angle-resolved X-ray photoelectron data.[15] It is a global minimum; i.e., of all

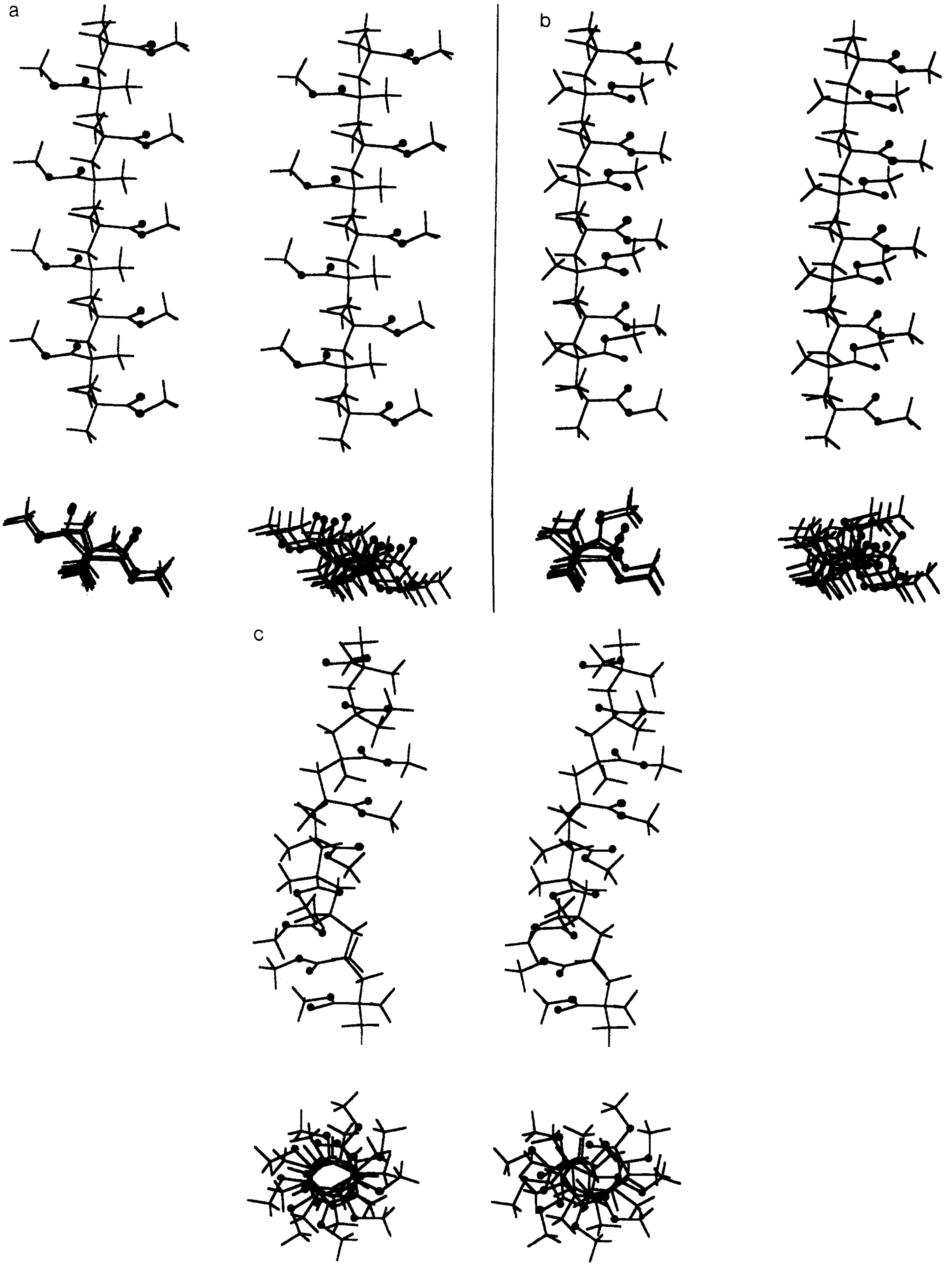


Figure 3. Minimum energy conformations of (a) linear (L) st-PMMA [cccc(c)cccc], (b) linear (L) it-PMMA [ctct(c)tctc], and (c) a right-handed 9/1 helix of it-PMMA [tttt(t)tttt]. Stereographic views into the long axis and along the axis in the bond model are shown.

possible minima, it has the lowest energy. The second minimum, shown in Figure 3c, is an approximate 9/1 right-handed (or left-handed) helix with a turn angle of 39°.

Because its relative minimum conformational energy is higher and the overall linear conformation has a smaller cross section and is assumed to be adsorbed and

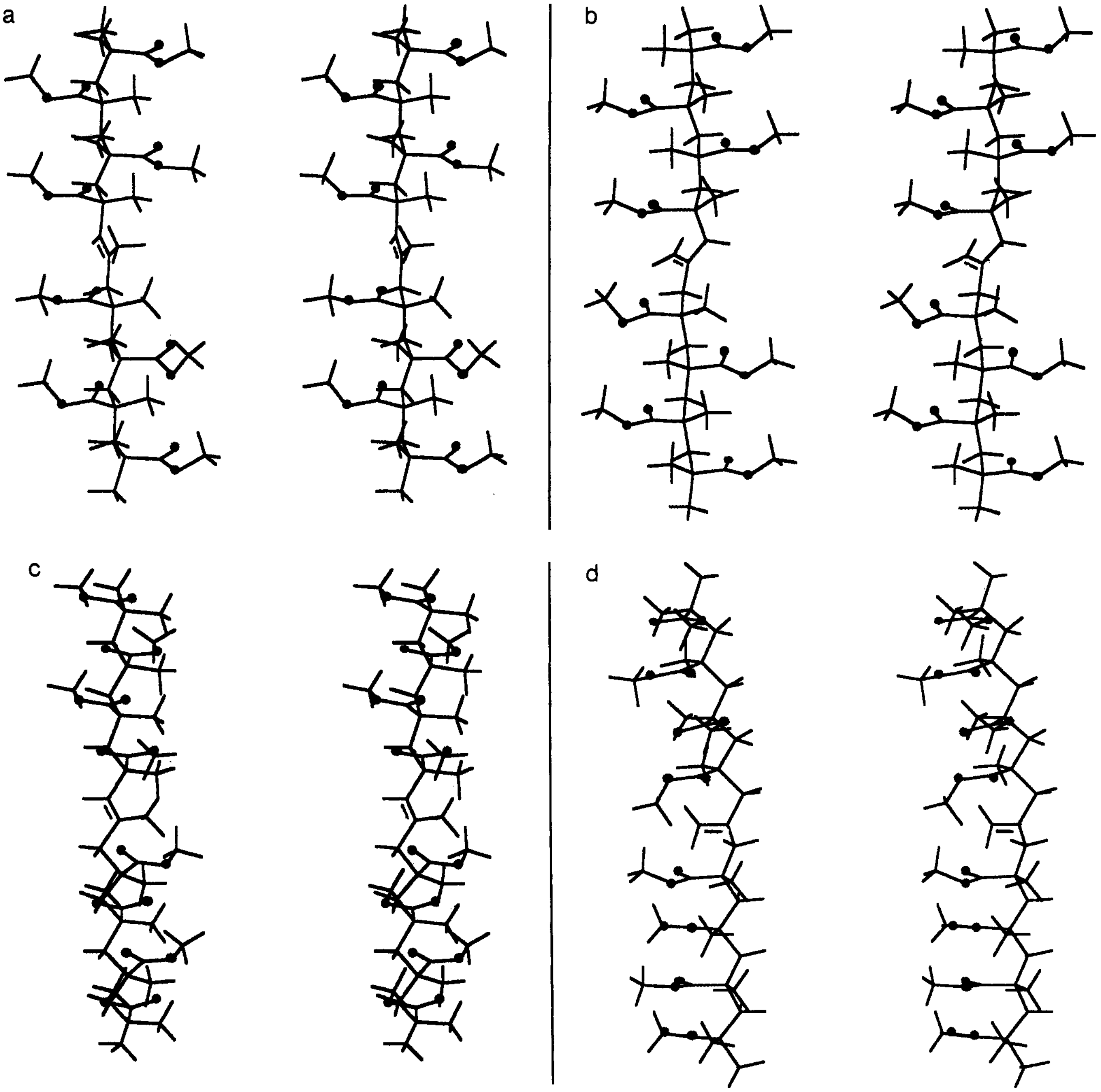


Figure 4. Minimum energy conformation of the linear (L) irradiated PMMA^d: (a) st-PMMA^d with [cccc(M=)cccc], (b) st-PMMA^d with [cccc(S=)cccc], (c) it-PMMA^d with [ctct(M=)tctc], and (d) it-PMMA^d with [ctct(S=)tctc] double bonds. Stereographic views into the long axis in the bond model are shown.

pack more effectively in the solid, the helical forms will not be used.

The photoproducts exhibit relative minimum energy conformations which we classify as overall linear and bent forms. Introducing a double bond and removing a methyl ester group reduces the intramolecular repulsion energy between the affected unit and its neighbors adjacent to the site of double bond formation. A global minimum energy conformation referred to as a bent (B) form for each of the (M=) and (S=) chain double bonds is found. We assume that this form is found in solution. If PMMA is constrained to the same overall linear (L) conformation as in the solid form, then a relative minimum for each of the M= and S= chain double bonds occurs with an overall linear conformation through the double-bonded region. We assume that this ordered form is retained in the solid after irradiation assuming that, for small extent of reaction, local mobility is not great enough to permit conformational reordering. Steric hindrance decreases more in the B than the L forms. The generation of an isolated double bond in a main chain sequence which is free to adopt the minimum energy structure requires a rather drastic change in the shape of the studied segment from linear to bent forms because of the change from sp^3 to sp^2 hybridization. If the irradiation process creates an excited state or species which can decay to generate MCS, S=, and M=, then the product distribution should be affected by the ease with which the required product may be attained. Thus, it is to be expected that, in the solid state, S= should be favored over M=, even though in small molecules the opposite is true.

Stereographic projections of st-PMMA^d in the all-cis and it-PMMA^d in the alternating cis–trans minimum energy linear and bent conformations are presented in Figures 4 and 5, respectively. These conformations are used in the subsequent analysis of double bond formation. An important finding in this analysis is that the minimum energy conformations of PMMA are linear for the st-isomer

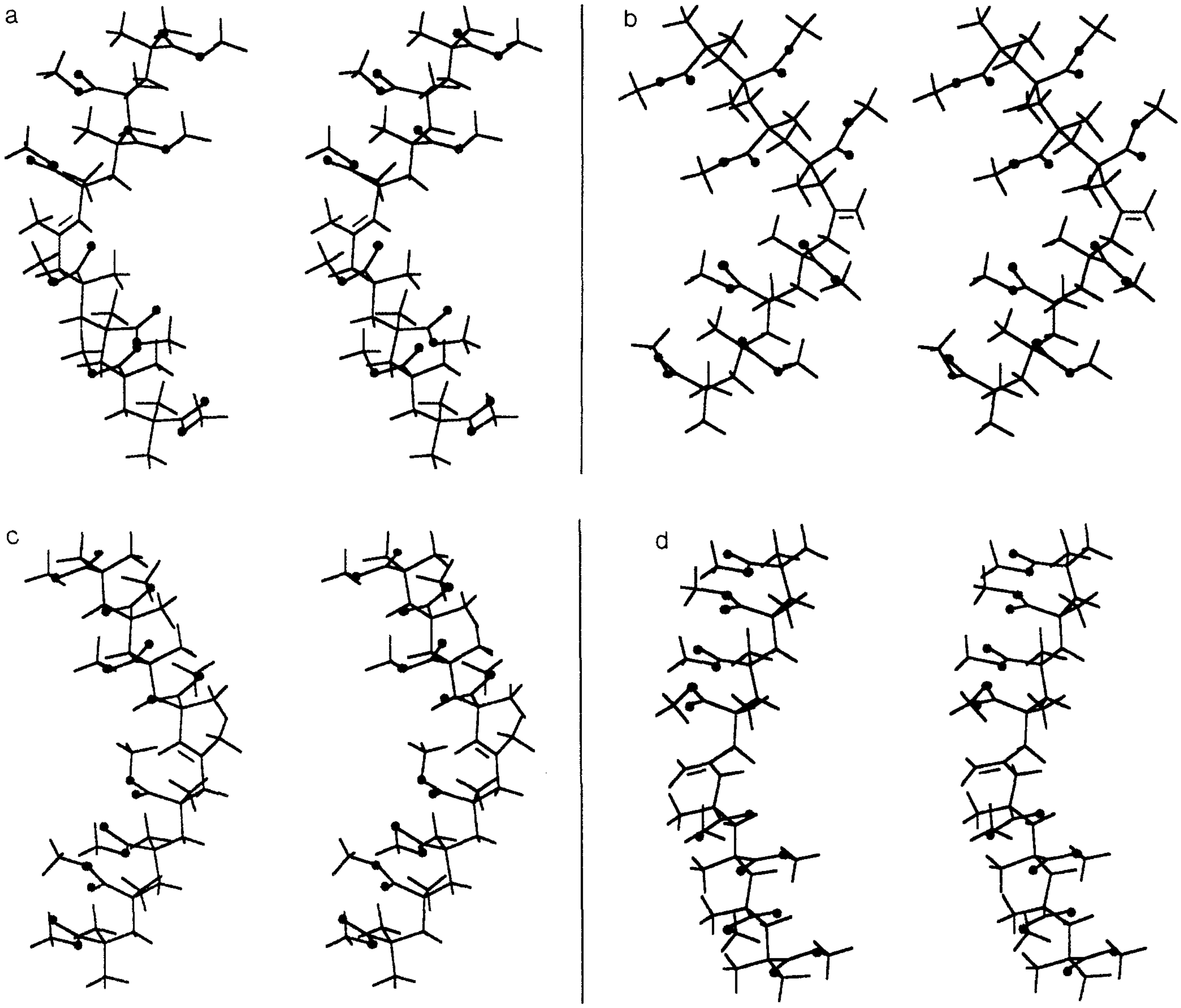


Figure 5. Minimum energy conformation of the bent (B) irradiated PMMA^d: (a) st-PMMA^d with [cccc(M=)cccc], (b) st-PMMA^d with [cccc(S=)cccc], (c) it-PMMA^d with [ctct(M=)tctc], and (d) it-PMMA^d with [ctct(S=)tctc] double bonds. Stereographic views into the long axis in the bond model are shown.

(3° kink in M= and S= formation) and 5.5° kink in M= formation and 20° kink in S= formation for it-PMMA^d. We assume that additional intermolecular stabilization will occur as the it-PMMA molecules pack into parallel linear chains in the solid state. The products of irradiation are assumed to remain in the matrix of the solid starting material and retain the overall linear conformations illustrated in Figure 4. If PMMA^d were generated in solution, all minimized energy conformations are expected, including the global minimum illustrated in Figure 5, which is found to be bent. Deposition of the bent form on a surface or in the crystal may accommodate the bent forms. Preliminary experiments indicate that the nature and concentration of PMMA^d generated in the solid are different from those observed in solution. We assume that once the solid has formed, the overall linear conformation of the polymer remains unaltered after irradiation; i.e., only a local conformational change at the site of irradiation occurs.

A preliminary analysis of the conformational energy as a function of chain length and presentation of the torsional angles of each polymeric form are presented elsewhere.[11] The reactions and the energy changes, calculated with a dielectric constant $\epsilon = 4$, of it- and st-PMMA proceeding to the product forms constrained to be linear yield the overall changes for st-PMMA (all trans) and it-PMMA (alternating cis–trans) as a result of irradiation:

$$\text{st-PMMA} \rightarrow \text{st-PMMA}^d(\text{L,M=})$$
$$\Delta E(\text{st,M=}) = -33.4\ (-20.4)\ \text{kcal/mol}$$

$$\text{st-PMMA} \rightarrow \text{st-PMMA}^d(\text{L,S=})$$
$$\Delta E(\text{st,S=}) = -82.0\ (-69.0)\ \text{kcal/mol}$$

$$\text{it-PMMA} \rightarrow \text{it-PMMA}^d(\text{L,M=})$$
$$\Delta E(\text{it,M=}) = +12.5\ (+25.5)\ \text{kcal/mol}$$

$$\text{it-PMMA} \rightarrow \text{it-PMMA}^d(\text{L,S=})$$
$$\Delta E(\text{it,S=}) = -28.0\ (-15.0)\ \text{kcal/mol}$$

An estimate of the total energy change is obtained by combining the conformational energy change (in parentheses) with the energy change due to double bond formation (discussed below). In this set of reactions, we consider the initial global minimum of the PMMA which can be laid on the surface without any further conformational change. PMMA is assumed to undergo local double bond formation without a substantial long-range change in the backbone conformation. Therefore this process is assumed to represent the chemical process on the surface. Side chain is favored over main chain double bond formation by 45.7 and 40.5 kcal for st- and it-PMMA^d production. In contrast, in solution no constraint on the backbone is present, and the PMMA^d can assume the global minimum of the bent conformations. If the reactions proceed to the bent forms, then the reactions

$$\text{st-PMMA} \xrightarrow{-33.4\ (-20.4)} \text{st-PMMA}^d(\text{L,M=}) \xrightarrow{(-92.2)} \text{st-PMMA}^d(\text{B,M=}) \qquad \Delta E(\text{st,M=}) = -125.6 \text{ kcal/mol}$$

$$\text{st-PMMA} \xrightarrow{-82.0\ (-69.0)} \text{st-PMMA}^d(\text{L,S=}) \xrightarrow{(-37.3)} \text{st-PMMA}^d(\text{B,S=}) \qquad \Delta E(\text{st,S=}) = -119.3 \text{ kcal/mol}$$

$$\text{it-PMMA} \xrightarrow{+12.5\ (+25.5)} \text{it-PMMA}^d(\text{L,M=}) \xrightarrow{(-67.7)} \text{it-PMMA}^d(\text{B,M=}) \qquad \Delta E(\text{it,M=}) = -55.2 \text{ kcal/mol}$$

$$\text{it-PMMA} \xrightarrow{-28.0\ (-15.0)} \text{it-PMMA}^d(\text{L,S=}) \xrightarrow{(-29.4)} \text{it-PMMA}^d(\text{B,S=}) \qquad \Delta E(\text{it,S=}) = -57.4 \text{ kcal/mol}$$

show that each isomer yields energy changes within 5 kcal/mol, which suggests that main chain double bond formation and side chain double bond formation of the bent forms are nearly the same energetically. The net change in energy due to double bond formation, $\Delta E = E(\text{C=C}) - 2E(\text{C–C})$,

$$\text{C[(CO}_2\text{CH}_3)(\text{CH}_3)]\text{CH}_2 \rightarrow \text{CH=C[CH}_3] + \text{HCO}_2\text{CH}_3 \qquad \Delta E(\text{M=}) = -13.0 \text{ kcal/mol}$$

$$\text{C[(CO}_2\text{CH}_3)(\text{CH}_3)]\text{CH}_2 \rightarrow \text{CH}_2[\text{C=CH}_2] + \text{HCO}_2\text{CH}_3 \qquad \Delta E(\text{S=}) = -13.0 \text{ kcal/mol}$$

for the main and side chain double bond formation is assumed to be the same. These values are obtained from a tabulation by Benson.[16] As an example, in the first reaction the total change (−125.6 kcal/mol) is obtained from the sum of energies for the double bond formation (−13.0 kcal/mol) plus the conformational change from Table I to account for the rearrangement of PMMA to the linear degraded PMMA^d (189.5 − 209.9 = −20.4 kcal/mol) form, followed by another conformational change of degraded PMMA^d from the linear to the bent form (97.3 − 189.5 = −92.2 kcal/mol). Alternative values $\Delta E(\text{M=}) = -4.0$ and $\Delta E(\text{S=}) = -4.0$ kcal/mol[17] for double bond formation may be used, but the overall trends in energetics remain the same.

Discussion and Conclusions

Of the three reactions considered here, MCS, M=, and S=, the solid phase or deposition on a surface favors S= over M= double bond formation because the constrained chain, assumed to be the linear conformation of the chain, is more stable. The results show an impact on the conformational energy resulting from conversion of a tetrahedral to a trigonal carbon atom. Because main chain scission results in increased solubility and incorporation of PMMA in a solid restricts the chain to linear conformations, degradation to M= is energetically less favorable. It is desirable to design derivatives of PMMA which attenuate or eliminate the undesirable S= reaction in the solid phase and therefore shift the distribution of products to MCS. Replacement of the α-methyl group by groups which are less likely to undergo hydrogen abstraction such as $\text{C[(CO}_2\text{CH}_3)(\text{CF}_3)]\text{CH}_2$ would be expected to accomplish this goal. The essential change is the replacement of hydrogen atoms at the position where abstraction occurs. Other compounds may be variants of this structure such as $\text{C[(CO}_2\text{CH}_3)(\text{CF}_3)]\text{CF}_2$. On the basis of the regular structure and overall linear conformations exhibited by the excluded volume studies,[11] we anticipate that larger group substitution cannot be accommodated by the present conformational analysis.

A search of the literature provides experimental support for the hypothesis advanced in this work. Pittman and co-workers[18–22] and others[23–26] have shown that the introduction of electron-withdrawing substituents into the α position of the methacrylate repeat unit modifies the response of that unit to incident radiation. Introduction of halogen atoms enhances chain cleavage but also increases the extent of cross-linking while incorporation of the trifluoromethyl group enhances the chain scission process without apparently generating cross-links.[25] Rationales put forward for these observations include the enhanced energy absorption of halogen atoms[22] and that the incorporation of halogen atoms might modify the radiation degradation process by providing favorable pathways for chain scission.[27] In an effort parallel to that of Pittman, Willson and co-workers studied poly(α-(trifluoromethyl)methacrylate) homopolymer and found it to be about twice as sensitive to electron beam irradiation as PMMA.[26] They also provided mechanistic insight into the enhanced cross-linking tendency of poly(α-fluoroacrylic ester) by hypothesizing that elimination of HF under irradiation forms in-chain double bonds (M= in our designation) which undergo cross-linking as the radiation dose increases. This hypothesis led them to the conclusion that replacing F with CF_3 would eliminate cross-linking because the absence of hydrogen atoms on the carbon atom β to fluorine would prevent double bond formation. They postulated that the enhanced scission yield observed when electron-withdrawing groups are introduced arises because of the stabilization of an initially generated backbone radical which eliminates an (also stabilized) acyl radical to form a terminal α-methyl vinyl end group. The increased stability of the proposed intermediates and the associated transition states would therefore favor the scission reaction. As described above, recent analyses of the NMR spectra of degraded PMMA have shown that other pathways for the generation of unsaturation (M= and S=) are also operative and that these pathways compete significantly with the scission reaction by destroying ester groups without causing chain scission. In fact, it appears from that work[2,28,29] that the sum of M= and S= is approximately 30 times as large as scission (MCS) for deep-UV irradiation. While the conclusions of Willson et al.[26] appear to remain valid, they can only be part of the explanation for the enhanced sensitivity. Replacement of CH_3 with CF_3 also prevents the elimination of hydrogen from the α-methyl group (the S= process) so that whatever the intermediate is that precedes elimination or cleavage, it has a greater chance to generate MCS in the CF_3 case than in the CH_3 case. It is also apparent that the physical state (solid vs solution) and tacticity have a marked influence on the outcome of the irradiation-induced processes.[3]

Most of the reactions leading to loss of ester groups (about 97%) in atactic PMMA film (which approximates a syndiotactic configuration) involved hydrogen abstraction from α-methyl and methylene groups leading to the generation of vinylidene groups (major) pendent from the chain and vinylene groups (minor) within the backbone, respectively. In contrast, films of isotactic PMMA or solutions of atactic PMMA exposed to deep-UV radiation yielded unsaturated bonds which had peak positions and intensities in the NMR spectra *different* from those found for irradiated atactic PMMA films. Work to elucidate further the apparent influence of stereochemistry and constraint in a solid matrix on the outcome of the photoprocesses operative in this system is currently underway.

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